PHYSICAL, CHEMICAL AND ISOTOPIC CHARACTERISTICS OF GROUNDWATER AND SURFACE WATER IN THE LAKE CHILWA BASIN, MALAWI

By

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Abstract

We measured the physical, chemical and isotopic properties of groundwater, streams and Lake Chilwa in the Lake Chilwa Basin in southern Malawi. Our goal was to assess water quality and identify the hydrogeochemical processes that control water quality. Groundwater in the Lake Chilwa Basin are highly saline which has led to water shortages because of poor water quality. We hypothesized that the highly saline groundwater resulted from water-rock interaction. The objective of the study was to assess the chemical evolution of the groundwater and surface water and their relationship to water-rock interactions. Groundwater from 16 boreholes, 5 stream water samples and 3 samples from Lake Chilwa were collected using standard methods and investigated for temperature, pH, electrical conductivity, total dissolved solids (TDS), major ions and stable isotopes of hydrogen and oxygen. Groundwater and Lake Chilwa water had higher ionic concentrations (e.g., HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}) than stream water. Ionic evolution models indicate weathering of silicate minerals as the major control of the ionic concentrations. The chemistry of water in the Lake Chilwa is markedly affected by evaporation. Concentrations of the TDS, HCO_3^- and Cl^- in many locations are above the recommended limits prescribed for drinking water by the World Health Organization (WHO). The results of this study show that the poor water quality is due to natural water-rock interactions. Because quality of streams water is adequate, and because base flow to perennial streams is supported by shallow groundwater, efforts should be made to map shallow fresh groundwater aquifers for domestic and industrial use.

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CHAPTER I

1.0 Introduction

Globally, groundwater and surface water are the major sources of water for domestic, agricultural and industrial purposes. Approximately one third of the world's population use groundwater for domestic use (Nickson et al., 2005). The World Health Organization (WHO) (2004) report that having safe drinking water is an internationally accepted human right. However, groundwater resources are under constant threat of salinization which is a worldwide concern (Rajmohan et al., 1997; Dar et al., 2011; Ebrahimi and Vilcáez, 2018a&b).

Groundwater and surface water in rural areas of Malawi are the source of water for domestic use (Southern Africa Development Corporation (SADC), 2002). A report by the British Geological Survey (BGS) (2004) indicates that groundwater in some parts of Malawi is characterized by high salinity as a result of evaporative concentration or dissolution of evaporative minerals in sedimentary rocks. The occurrence of groundwater with high salinity in southern Malawi is a major water quality problem (Davis, 1969; Monjerezi, 2011). The Lake Chilwa Basin in southern Malawi has saline ground water and surface waters and water use is impaired by high concentrations of solutes (Food and Agricultural Organization (FAO), 2005). Boreholes which tap groundwater with high salinity are frequently abandoned in favor of open unprotected shallow hand dug holes in

dry river beds or surface water (Bath, 1980). High levels of other physico-chemical and microbiological parameters (EC, TDS, turbidity, fecal coliform and fecal streptococci) at several sites suggest that the water sources are grossly contaminated with bacteria, hence not suitable for human consumption without treatment (Chidya et al., 2016).However, the expansion of groundwater supplies countrywide and the improvement of drinking water quality remains a national priority (Government of Malawi (GOM), 1995).

Previous investigations of the quality of groundwater and surface water in the Lake Chilwa Basin focused on determining the physical properties and concentrations of chemical and biological pollutants and their conformance with WHO and Malawi Bureau of Standards (MBS) drinking water quality guidelines (Saka and Ambali, 1999;Palamuleni, 2002;Msonda et al., 2007; Hellen, 2013).Although borehole supplies are used by a significant percentage of the population in Malawi, information on the chemical composition of the water in these boreholes is either scanty or non-existent (Bath, 1980; Chilton and Smith Carington, 1984; Mc Farlane and Bowden, 1992; Kanyerere, et al., 2010; Palamuleni, 2002; Sajidu et al., 2008; Chidya et al., 2016).There are no dedicated studies on the hydro-geochemical properties designed to understand the processes that add solutes into or remove solutes from groundwater and surface water in the Lake Chilwa Basin.

Geochemical processes occurring within the groundwater and surface water and reactions with aquifer minerals have a profound effect on water quality. These geochemical processes are responsible for the temporal and spatial variations in groundwater and surface water chemistry. Where there are marked and temporal variations in the physical and

chemical properties of groundwater and surface water, tracing these changes relative to the water cycle is instructive in understanding the chemical evolution. Stable oxygen ($\delta^{18}O$) and hydrogen isotopes (δD) have proven very useful in tracing the water cycle and in the understanding of hydro-chemical evolution of groundwater and surface water (Gat and Tzur, 1968; Fontes et al., 1980).

The $\delta^{18}O$ and δD of water can be used as an effective tracer of rain recharge, groundwater flow, water-rock interaction and evaporative processes (e.g., Fritz and Clark, 1997). The fact that the previous studies in the Lake Chilwa Basin did not use stable isotopes of water and hydro-geochemical processes to understand the chemical evolution of water in relation to water quality is a major knowledge gap in our understanding of the origin of water quality in the Lake Chilwa Basin.

The overarching goal of this study is to understand the origin of water quality in the Lake Chilwa Basin, by developing a fundamental understanding of the dominant geochemical processes responsible for groundwater and surface water quality. We hypothesize that highly saline groundwater in the Lake Chilwa Basin results from water-rock interactions. The objective of this study was to assess the origin of the quality of groundwater and surface water from physical, chemical and isotopic properties. We used a combination of the physical properties, the major ion concentrations and $\delta^{18}O$ and δD of water and their relation to water-rock interaction to fulfill our objective.

The results of this study is useful to bridge the information gap needed in addressing groundwater and surface water quality, as well as providing a foundation for groundwater monitoring. Groundwater monitoring is important as it provides groundwater quality

information, such as identification of specific chemical species and associated concentrations that impair groundwater and surface water quality. Such information can help decision makers better understand the water quality and their potential effects on public health and the ecosystem, and how to address issues of water quality impairment.

CHAPTER 2

2.0 Study Area

2.1 Location

Lake Chilwa Basin (latitude 15º 20'S, longitude 35º 40'E) is a close basin of about 7500km^2 located in the southern Malawi and includes portion of north eastern Mozambique as shown in Figure 1.

The Lake Chilwa Basin covers three administrative districts: Phalombe has about 73,880 hectares, Machinga has about 11,200 hectares and Zomba has about 185,174 hectares of land (Sagona, 2016). The Lake Chilwa Basin is bounded to the west by the Chikala Hills, Zomba and Malosa Mountains, the Shire highlands and Chiradzulu Mountain. These highlands give rise to the Domasi River, Likangala River, Thondwe River and Namadzi River. The basin is bounded to the south-east by the Mulanje and Michesi mountains which give rise to the Phalombe River and Sombani River. To the east lie the hills and mountains of Mozambique which give rise to Mnembo River and Mbugwe River (Njaya, 2011). Among the seven rivers only Domasi River and Likangala River are perennial, the rest dry up during the dry season.

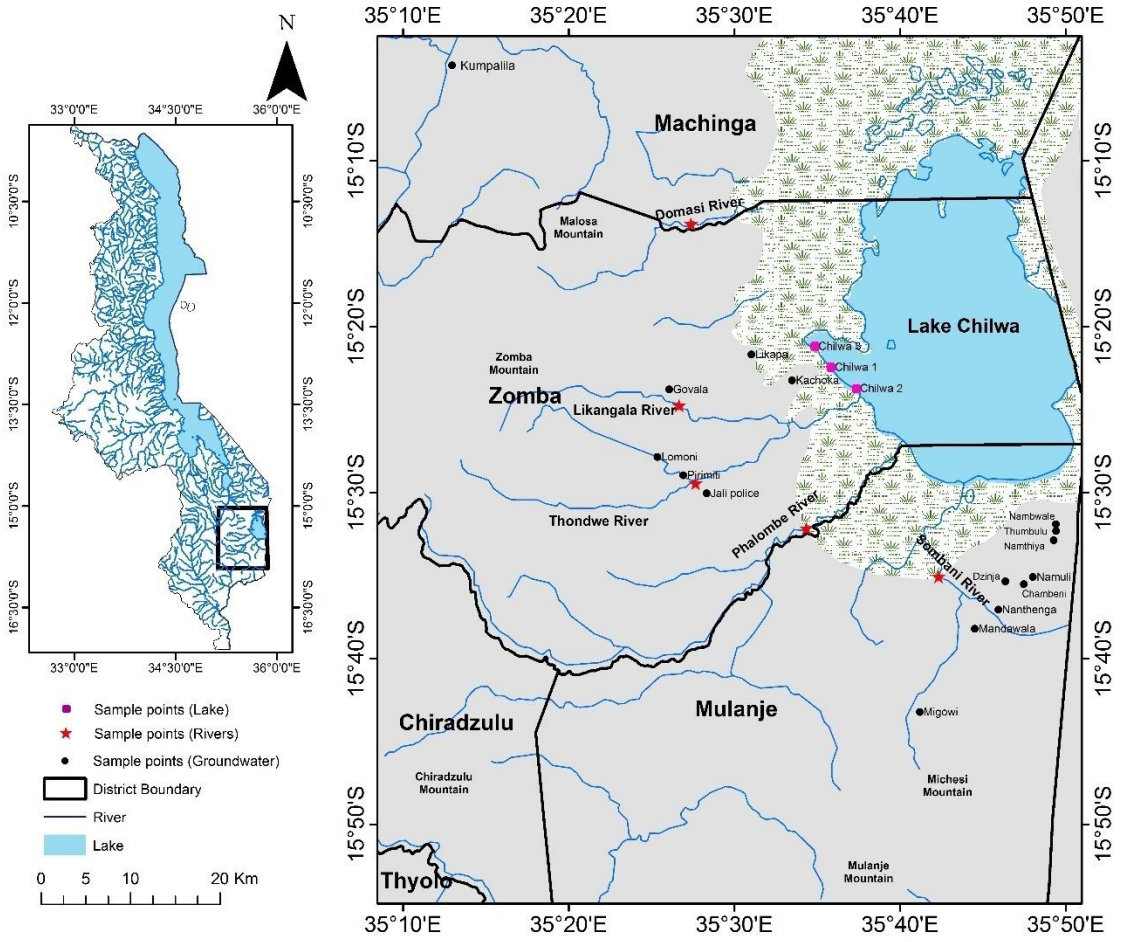


Figure 1 Map of Malawi showing river drainage; the solid rectangle is the location of the study area. The map shows Lake Chilwa and groundwater and surface water sampling locations. Shape files provided by Geological Survey Department, Malawi.

2.2 Topography and geology

The topography of the Lake Chilwa Basin is made up of uplands and lowlands (Figure2). The Lake Chilwa Basin is a tectonic depression of post-cretaceous age that has been progressively filled with sand, silt and various sediments from the denudation of the surrounding highlands (Sagona, 2016).The uplands have deep, well drained sandy soils

derived from the weathering of gneisses, while the lowlands have very deep soils with variable drainage in fluvial, colluvial and lacustrine deposits (Morgan and Kalk, 1970).

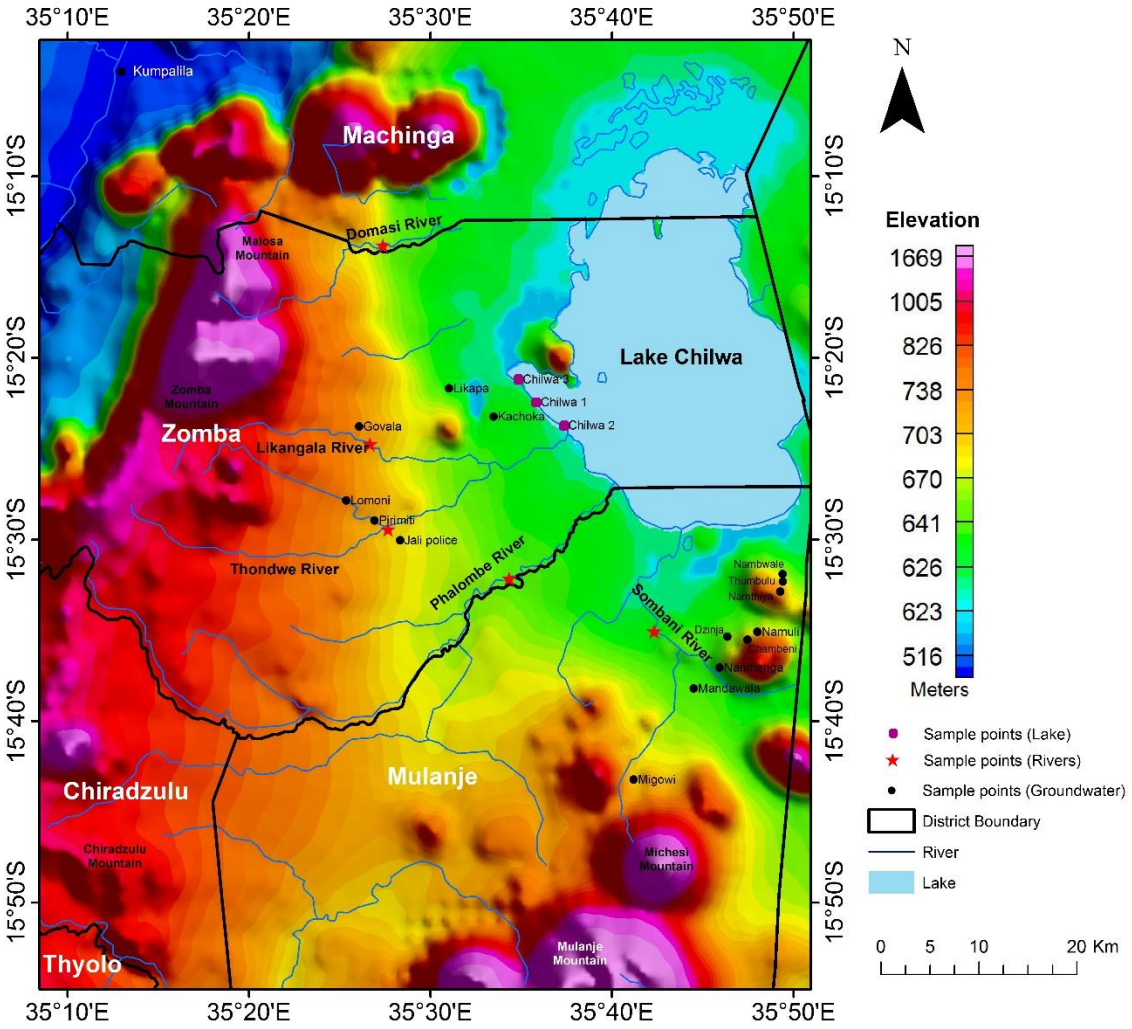


Figure 2:Digital elevation map of the study area. Source: ETOPO1 Global Elevation data.

The Lake Chilwa Basin as shown in Figure 3 is characterized by (1) crystalline metamorphic and igneous rocks of Precambrian to lower Paleozoic age referred to as the basement complex (Carter and Bennett, 1973; Chilton and Smith-Carington, 1984; Mapoma and Xie, 2014). The major lithological units of the basement complex are

charnockites and granulites. Charnockites include orthopyroxene granite, quartz, feldspar, syenite and others, whereas granulites include pyroxene, biotite, garnet, calcium plagioclase and quartz, (2) the Chilwa alkaline intrudes the Precambrian basement and is divided into 4 lithological units: basanite, granite and syenite, nepheline syenite and carbonatite. Nepheline syenite (sodium potassium aluminosilicate) consists largely of nepheline and alkali feldspars which include microcline, albite, mica, hornblende and magnetite.

Carbonatites consists of calciocarbonate, magnesiocarbonate and ferrocarbonate, (3) Cenozoic sediments consisting of alluvial fans and lacustrine sediments. Intrusions of carbonatites in the Chilwa Alkaline Province have formed features that define the topographic ring complex of Zomba and Mount Mulanje (Swanzie and Stubbs, 1972). The study by Swanzie and Stubbs (1972) show that the carbonatites contain rare earth elements, apatite, limestone and marble. Bloomfield (1965) states that the major rock types of the Lake Chilwa Basin are charnockitic gneiss and granulite. These rocks are characterized by the development of north-north-east (N-N-E) trending foliations.

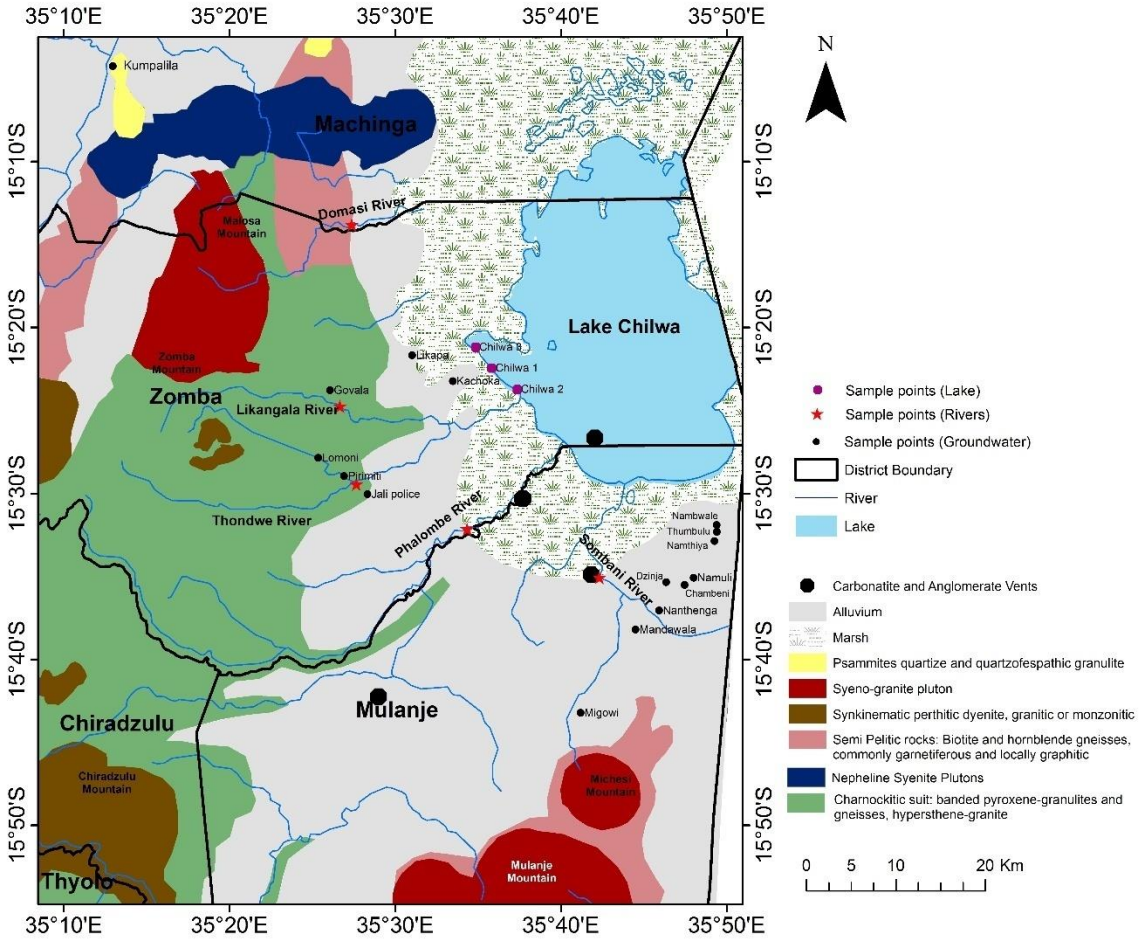


Figure 3: Geological map of the study area. Source: Geological Survey Department of Malawi.

2.3 Climate and hydrology

The Lake Chilwa Basin experiences a warm tropical climate, which is characterized by rainy and dry seasons. The rainy and dry seasons occur from November to April and May to October, respectively. The mean annual temperature is 24ºC. The highest temperature of 29ºC and the lowest temperature of 20ºC are experienced in October and June, respectively (Government of Malawi (GOM), 2010).

Rainfall variability has a significant impact on water availability and the discharge particular catchments (McCarthy et al., 2001; Bloomfield, 2002; Ngongondo, 2006; Mapoma and Xie, 2014). However, processes other than rainfall play a significant role in the hydrologic processes of any catchment (Ngongondo, 2006). The numerous rivers, lakes, dams, lagoons and marshes existing in Malawi (GOM, 2011) connect with groundwater in either recharge zones or in discharge zones.

The drainage pattern of the Lake Chilwa basin is radial (Figure 2) (Lancaster, 1981).Lake Chilwa is at an altitude of 650 m above mean sea level (amsl). The maximum depth of the lake is 2.7 m and the lake surface measures 1759 km^2. There are six major influent rivers draining into Lake Chilwa: the Domasi, Likangala, Thondwe, Phalombe, Sombani and Mnembo with maximum discharges which occur during the rainy season of December to April, usually peaking in February (Lancaster, 1979). The Mnembo River flows from Mozambique into Lake Chilwa and is actually the lake's largest source of water (Jamu et al., 2003).

The aquifers hosting groundwater in the Lake Chilwa Basin include the deeper basement aquifers and shallow sedimentary alluvial aquifers (Mapoma and Xie, 2014). The basement aquifers are low yielding because of the less porous nature of igneous and metamorphic rocks that do not allow a lot of water to pass through them whereas shallow alluvial aquifers are high yielding.The water table is closer to the surface in the valley region and deeper in higher elevations (Mkandawire, 2004). Borehole yields are highest where saturated thickness of the weathered zone is greatest (Chilton and Smith-Carington, 1984). In general, however, the weathered basement aquifer produces low groundwater yields

(GOM, 2007; Chilton and Smith-Carington, 1984). On the other hand, shallow alluvial aquifers are high yielding with recorded yields in excess of 10 L/s (Chimphamba et al., 2009; GOM, 2007). Mc Farlane et al. (1992) observed and concluded that very flat land at least one kilometer from the hill or mountain is generally likely to be high yielding than sites close to the hill. In terms of chemistry, the shallow aquifers are less mineralized than the deeper aquifers (Mc Farlane and Bowden, 1992). Groundwater is of variable qualities and quantities, unevenly distributed in time and space (GOM, 2007). Aquifer recharges from broad interfluves and groundwater discharges in surface depressions.

CHAPTER 3

3.0 Methodology

3.1 Sample collection

Water samples were collected from boreholes, streams and Lake Chilwa using standard sampling procedures (APHA, 1985). Water sample collection was conducted from 20th December, 2016 to 2nd January, 2017. Groundwater samples were collected from the following boreholes: Dzinja, Namthiya, Nthumbulu, Nambwale, Namuli, Chambeni, Nanthenga, Mandawala, Migowi, Likapa, Govala, Kachoka, Pirimiti, Jali police, Lomoni and Kumpalila (Figure1). Groundwater samples were collected by hand pumping after purging three estimated casing volumes.

All stream water samples were collected in easily accessed points (e.g., under bridges) from the following streams: Domasi, Likangala, Thondwe, Phalombe and Sombani. Lake water samples were collected from the western side of Lake Chilwa along the shore from three locations (Figure1). Stream water and lake water samples were collected using grab technique.

All water samples were filtered through a 0.45 µM nylon filter during collection. The sample bottles were rinsed three times with the filtered water sample to be collected and then filled and capped. Filtered water for cations analysis were collected in 60 mL polypropylene bottles, acidified to a pH < 2 with high purity nitric acid (Apha, 1989), and stored in cooler box. Samples for anions and silica analyses were collected unacidified in 30 mL polypropylene bottles and stored in a cooler box. Water samples for dissolved inorganic carbon(DIC) were collected using syringes and introduced into septum tubes pre-loaded with 1.5 mL of 85% phosphoric acid and magnetic stir bars as described by Atekwana and Krishnamurthy (1998).

3.2 Measurements and sample analysis

Water temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in situ at each borehole during purging using potable multi-meter probe (HANNA instrument model 991300N). The probe of the meter was dipped in the container receiving the pumped water and readings were taken after stabilization (Apha, 1989). For surface water, the probe was immersed in the water and readings are recorded after stabilization.

In the field, alkalinity was determined by H_2SO_4 titration to an acid equivalent point of 4.2 using a digital titrator (Hatch Company, 1992). Dissolved silica was measured using heteropoly blue chemistry to determine the "molybdate reactive" silica and measured with a CHEMetrics V-2000 Photometer at 815 nm (CHEMetrics, 2012). In the laboratory, major anions and cations (F^-, Cl^-, SO_4^{2-}, NO_3^- and Na^+, K^+, Ca^{2+}, Mg^{2+}) were determined by ion chromatography. Dissolved inorganic carbon concentrations were determined by

extraction and cryogenic purification of carbon dioxide ($CO_{2(g)}$) using a vacuum line and $CO_{2(g)}$ (Atekwana and Krishnamurthy, 1998). Stable isotopes of hydrogen and oxygenanalysis of water samples was done using Off Axis-Integrated Cavity Output Spectroscopy (OA-ICOS) manufactured by Los Gatos and sold as the Triple Liquid Water Analyzer. Stable isotopes ratios for hydrogen and oxygen are reported in the delta (δ) notation in per mil (‰):

$$\delta(‰) = ((R_{sample}/R_{standard}) - 1) \text{ X } 1000$$

where R is $^{2}H/^{1}H$ or $^{18}O/^{16}O$. The δ values for H and O isotopes are reported relative to the Vienna Standard Mean Ocean Water (VSMOW). Routine isotopic measurements of in-house standards and samples have an overall precision of 0.2 and 1 ‰ for oxygen and hydrogen, respectively.

3.3 Determination of watertypes and mineral saturation indices

The results of the physical-chemical analysis were uploaded to AquaChem where water types were determined. Phreeqc version 2 was used to calculate mineral saturation indices and the partial pressure of CO_2(pCO_2) using pH, DIC, $Ca^{2+}$and temperature (Parkhurst and Appelo, 1999).

CHAPTER 4

4.0 Results

4.1 Physical parameters

Summary statistics of the results are presented in Table 1, while results of the physical, chemical and isotopic parameters are presented in Table 2.The pH of groundwater ranged from 6.8 to 7.2 and averaged 6.9±0.2. The pH of lake water samples was more alkaline which ranged from 8.4 to 8.8 and averaged 8.6±0.2. Stream water samples had an average pH of 7.5±0.2 and ranged from 7.4 to 7.9.

Table 1: Summary statistics of the physical and chemical compositions of water samples. All values are in mg/L except pH, temperature (°C), electrical conductivity (EC) (µS/cm) and oxygen isotope ($\delta^{18}O$) and hydrogen isotopes (δD)(‰). GW is groundwater, LW is lake water, SW is stream water, Minis minimum value, Max is maximum value and SD is the standard deviation.

		pH	Temp	EC	TDS	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	SiO_2	$\delta^{18}O$	δD
GW	Min	6.8	27.1	1563	1000	52.2	0.4	13.9	36.4	0.8	21.3	27.3	0.2	286.0	74.0	-6.3	-39
	Max	7.2	30.1	3497	2238	149.9	3.4	42.1	122.4	39.5	134.7	59.3	21.9	428.0	110.0	-4.7	-28
	Mean	6.9	28.1	2450	1568	92.8	1.5	28.9	79.8	11.1	78.5	41.4	6.2	344.7	91.5	-5.8	-35
	SD	0.2	0.9	604	387	33.3	0.9	7.1	25.2	11.8	38.1	12.3	6.1	40.7	9.4	0.5	3
LW	Min	8.4	27.3	3001	1921	319.0	12.0	6.0	17.4	40.4	320.3	14.1	17.0	253.0	91.0	7.5	33
	Max	8.8	27.8	3589	2297	338.0	12.7	10.7	20.6	42.0	363.2	18.8	19.7	297.1	93.0	9.5	45
	Mean	8.6	27.5	3313	2121	328.4	12.4	7.9	19.0	41.4	343.0	16.3	18.2	275.5	92.0	8.5	40
	SD	0.2	0.3	296	189	9.5	0.4	2.3	2.0	0.9	22.0	2.4	1.4	22.1	1.0	0.5	6
SW	Min	7.4	22.3	1350	553	10.6	3.0	1.3	1.8	0.6	2.4	4.0	0.5	26.2	47.0	-4.8	-30
	Max	7.9	29.5	1489	610	42.2	12.4	2.3	3.5	2.6	8.1	12.6	10.4	111.0	89.0	3.5	-14
	Mean	7.5	23.3	1445	592	23.3	4.6	1.7	2.5	2.0	5.4	10.4	2.9	63.1	74.0	0.2	-16
	SD	0.2	3.2	58	23	11.6	3.3	0.5	0.6	0.8	2.3	3.6	4.2	34.9	16.0	3.3	20

The temperature of groundwater, lake water and stream water samples ranged from 27.1 to 30.1°C, 27.3 to 27.8°C and 22.3 to 29.5 °C, respectively and averaged 28.1±0.9, 27.5±0.3 and 26.4±3.2 °C, respectively. For groundwater the EC averaged 2450±604

µS/cm and ranged from 1563 to 3497 µS/cm. For the lake water samples and stream water samples, the EC ranged from 3001 to 3589 and 1350 to 1489µS/cm, respectively and averaged 3313±296 and 1445±58 µS/cm, respectively. The conductance of the stream water samples might be higher than those obtained by Saka (2006) and I attribute this to be so due to time and space. I collected my samples at the beginning of the rainy season when evaporation has occurred and the volume of water has greatly reduced causing the water to be highly concentrated.

Table 2: Results of the physical, chemical and isotopic analyses of water samples from Lake Chilwa Basin (- = not measured).

SampleID	StationID	pH	Temp. (°C)	EC (µS/cm	TDS (ppm)	Na^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)	SiO_2 (ppm)	DIC (mg C/l)	$\delta^{18}O$ (‰)	δ^2H (‰)	SI calcite	SI dolomite	SI gypsum	pCO_2 (atm)
Pt 1 BH	Dzinja	6.88	27.1	2861	1831	149.9	0.7	28.9	122.4	25.4	134.7	37.7	2.6	417.9	74	115	-6.3	-38	-0.4	-0.7	-2.9	-4.3
Pt 2 BH	Namthiya	6.84	27.3	2780	1779	126.2	1.7	34.1	119.2	5.56	130.3	35.4	9.5	488.0	99	189	-6.3	-37	-0.2	-0.6	-2.7	-4.4
Pt 3 BH	Thumbulu	6.93	30.1	2869	1836	138.2	2.7	19.3	88.8	15.2	132.6	57.4	10.3	381.9	79	121	-6.1	-35	-0.1	-0.6	-2.6	-4.3
Pt 4 BH	Nambwale	6.78	28.9	1948	1247	115.7	0.8	36.7	122.2	11.4	129.3	59.3	13.5	341.6	93	109	-6.0	-35	-0.1	-0.6	-2.7	-4.2
Pt 5 BH	Namuli	6.71	28.2	3497	2238	95.0	2.1	42.1	80.0	32.1	104.5	41.6	6.8	390.3	95	148	-6.0	-36	0.0	-0.2	-2.8	-4.6
Pt 6 BH	Chambeni	7.10	28.9	3206	2052	128.7	1.8	25.8	76.4	17.1	96.8	56.7	9.5	357.1	101	199	-6.1	-38	-0.2	-0.5	-2.7	-5.5
Pt 7 BH	Nanthenga	6.85	28.5	2815	1802	130.7	1.7	32.4	100.2	39.5	76.0	28.9	1.3	313.9	103	210	-5.9	-36	-0.2	-0.6	-3.8	-4.3
Pt 8 BH	Mandawala	7.11	29.8	3100	1984	61.7	1.9	33.9	66.2	5.8	62.6	59.0	4.7	326.4	110	208	_	_	-0.2	-0.4	-3.0	-4.5
Pt 9 BH	Migowi	6.82	27.9	1755	1123	82.2	1.8	13.9	68.4	1.1	47.8	58.6	1.1	322.4	95	146	_	_	-0.4	-1.0	-3.7	-4.3
Pt 10 BH	Likapa	7.06	27.6	1563	1000	75.7	0.4	28.0	80.4	3.1	77.2	31.4	0.3	286.0	84	131	_	_	-0.5	-0.8	-4.3	-4.4
Pt 11 BH	Govala	6.79	27.0	1610	1030	66.9	2.0	20.2	67.5	0.8	61.4	34.6	0.8	316.8	91	135	-5.6	-33	-0.5	-1.1	-3.9	-4.1
Pt 12 BH	Kachoka	6.88	28.0	2359	1510	62.6	0.2	26.7	52.4	2.8	33.2	37.2	1.6	340.6	90	133	-4.7	-28	-0.4	-0.7	-3.7	-4.3
Pt 13 BH	Pirimiti	6.95	27.3	1962	1256	52.2	0.9	33.2	68.4	1.8	44.8	37.4	0.2	300.6	82	129	-5.0	-31	-0.4	-0.7	-4.4	-4.4
Pt 14 BH	Jali police	7.11	27.8	2680	1715	77.1	0.4	25.3	36.4	5.7	54.5	29.9	11.3	314.7	92	140	-5.9	-39	-0.3	-0.6	-2.7	-0.6
Pt 16 BH	Lomoni	6.70	27.4	2200	1408	52.7	3.4	33.9	71.6	5.6	49.6	27.3	3.0	336.0	83	127	_	_	-0.4	-0.6	-3.3	-3.9
Pt 17 BH	Kumpalila	7.22	27.5	1990	1274	69.9	1.6	27.7	55.6	4.7	21.3	29.3	21.9	341.6	93	142	_	_	-0.6	-0.8	-2.7	-4.6
Pt 1 SW	L. Chilwa	8.41	27.8	3589	2297	328.1	12.7	10.7	20.6	40.4	363.2	18.8	19.7	276.5	93	98	9.5	45	-1.3	-2.0	-5.9	-5.3
Pt 7 SW	L. Chilwa 2	8.78	27.5	3350	2144	338.0	12.4	7.1	19.0	42.0	345.5	16.0	18.0	297.1	92	106	8.5	33	-1.0	-2.2	-3.4	-5.5
Pt 8 SW	L. Chilwa 3	8.63	27.3	3001	1921	319.0	12.0	6.0	17.4	41.8	320.3	14.1	17.0	253.0	91	94	7.5	21	-1.4	-2.5	-2.6	-5.4
Pt 2 SW	Phalombe R	7.52	28.8	915	586	42.2	3.0	1.3	1.8	2.6	8.1	4.0	10.4	111.0	78	85	3.5	18	-2.2	-4.3	-4.0	-4.9
Pt 3 SW	Sombani R	7.42	23.8	949	607	22.9	4.4	2.3	3.3	0.6	6.1	12.6	1.1	86.6	82	86	0.5	-25	-2.6	-5.2	-5.5	-4.8
Pt 4 SW	Thondwe R	7.93	29.5	941	602	20.5	3.9	2.3	2.3	2.6	6.6	11.7	1.3	39.7	77	78	2.8	-14	-2.5	-4.9	-4.7	-5.1
Pt 5 SW	Likangala R	7.35	27.4	864	553	20.2	3.1	2.1	2.5	2.2	3.8	11.3	1.4	51.9	89	88	-1.0	-27	-1.9	-4.1	-4.2	-4.7
Pt 6 SW	Domasi R	7.32	22.3	953	610	10.6	2.5	1.3	2.8	2.1	2.4	12.4	0.5	26.2	73	80	-4.8	-30	-1.8	-4.9	-4.4	-4.6

For all the groundwater samples, the average TDS concentration was 1568±387 mg/L and ranged from 1000 to 2238 mg/L. TDS concentration for Lake Chilwa samples averaged 2121±189 mg/L and ranged from 1921 to 2297 mg/L. For Stream water samples, the TDS averaged 592±23 and ranged from 553 to 610 mg/L. The EC and TDS results of the Lake Chilwa water seems to be much higher than those of groundwater and fresh stream water samples. This is because the lake is a sink without a surface outlet for all sediments from catchment rivers and run-offs (Mumba et al.,1999;Saka, 2006).However, the TDS concentration shown in table 2 is the measured TDS, which includes all the dissolved solutes contained in the water

4.2 Chemical parameters

Among the cations, the concentrations of Na^+, K^+,$Mg^{2+}$and Ca^{2+} for groundwater ranged from 52.2 to 149.9, 0.4 to 3.4, 13.9 to 42.1 and 36.4 to 122.4 mg/L and averaged 92.8 ± 33.3, 1.5 ± 0.9, 28.9 ± 7.1 and 79.8 ± 25.2 mg/L, respectively. For lake water, the concentrations of Na^+, K^+,$Mg^{2+}$and Ca^{2+} ranged from 319.0 to 338.0, 12.0 to 12.7, 6.0 to 10.7 and 17.4 to 20.6 mg/L and averaged 328.4±9.5, 12.4±0.4, 7.9±2.3 and 19.0±2.0 mg/L, respectively. For stream water samples, the concentrations of Na^+, K^+,$Mg^{2+}$and Ca^{2+} ranged from 10.6 to 42.2, 3.0 to 12.4, 1.3 to 2.3 and 1.8 to 3.5 mg/L and averaged 23.3±11.6, 4.6±3.3, 1.7±0.5 and 2.5±0.6 mg/L, respectively. The order of abundance of the cations for the groundwater and the lake water samples is Na^+> Ca^{2+}> Mg^{2+}> K^+ and Na^+> Ca^{2+}>K^+>Mg^{2+}, respectively. The order of abundance of the cations for the stream water samples is Na^+>K^+>Ca^{2+}>Mg^{2+}.

For the anions, groundwater concentrations ofF^-,Cl^-,NO_3^-,SO_4^{2-} and HCO_3^- ranged from 0.8 to 39.5, 21.3 to 134.7, 27.3 to 59.3, 0.2 to 21.9 and 286.0 to 428.0 mg/L, respectively and averaged 11.1 ± 11.8, 78.5 ± 38.1, 41.4 ± 12.3, 6.2 ± 6.1 and 344.7 ± 40.7 mg/L, respectively. For lake water samples the concentrations ofF^-,Cl^-,NO_3^-,SO_4^{2-} and HCO_3^- were between 40.4 to 42.0, 320 to 363, 14.1 to 18.8, 17.0 to 19.7 and 253.0 to 297.1 mg/L, respectively and averaged 41.4±0.9, 343±22, 16.3±2.4, 18.2±1.4 and 275.5±22.1 mg/L, respectively. For stream water samples the concentrations ofF^-,Cl^-,NO_3^-,SO_4^{2-} and HCO_3^- ranged from 0.6 to 2.6, 2.4 to 8.1, 4.0 to 12.6, 0.5 to 10.4 and 26.2 to 111.0 mg/L, respectively and averaged 2.0±0.8, 5.4±2.3, 10.4±3.6, 2.9±4.2 and 63.1±34.9 mg/L, respectively. The order of abundance is $HCO_3^->Cl^->NO_3^->F^- >SO_4^{2-}$, $Cl^->HCO_3^->F^->SO_4^{2-}>NO_3^-$and $HCO_3^->NO_3^->Cl^->SO_4^{2-}> F^-$ for groundwater, lake water and stream water samples, respectively.

The concentration of SiO_2 in groundwater, lake water and stream water samples averaged 91.5±9.4, 92.0±1.0 and 74.0±16.0 mg/L and ranged from 74.0 to 110.0, 91.0 to 93.0 and 47.0 to 89.0 mg/L, respectively. The concentration of Na^+, K^+, F^-, Cl^-, SO_4^{2-} and SiO_2 is highest in the lake water samples than in groundwater samples and stream water samples due to same reason that Lake Chilwa is a sink with no outlet (Saka, 2006).

4.3 Isotopic parameters

The $\delta^{18}O$ ratios for groundwater, lake water and stream water ranged from -6.3 to -4.7, 7.5 to 9.5 and -4.8 to 3.5‰, respectively and averaged -5.8±0.5, 8.5±0.5 and 0.2±3.3‰, respectively. The δD ratios for groundwater, lake water and stream water range from -39 to -28, 7 to 33 and -30 to 18 ‰, respectively with averages of -35±3, 20±18 and -16±20

‰, respectively. Groundwater samples show more negative values of both $\delta^{18}O$ and δD, whereas, lake water samples show the most positive values and stream water samples show intermediate values.

CHAPTER 5

5.0 Discussion

5.1 Water quality of groundwater and surface water

The quality of groundwater and surface water determines its suitability for different purposes depending upon specific standards. The drinking water standards (Table 3) of the WHO (2008) and the Malawi Bureau of Standards (MBS) (MBS, 2005) was the basis for the water quality evaluation.

Table 3: Water Quality Standards. World Health Organization (WHO) Drinking Water Guidelines (WHO, 2008) and Malawi Bureau of Standards (MBS) Maximum Permissible Levels (MBS, 2005).

Constituent	Unit	WHO Guideline	MBS Guideline
Total dissolved solid (TDS)	mg/L	1000	1000
Sodium	mg/L	Not stated	200
Potassium	mg/L	10	10
Magnesium	mg/L	150	150
Calcium	mg/L	200	200
Fluoride	mg/L	1.5	2
Chloride	mg/L	250	250
Nitrate	mg/L	50	50
Sulfate	mg/L	400	400
Bicarbonate	mg/L	300	Not stated

The pH values of groundwater in the Lake Chilwa Basin averaged 6.9±0.2 which indicates slightly acidic and pH of lake water and stream water with the means of 8.6±0.2 and 7.5±0.2, respectively indicates that the lake water and surface water are alkaline. The pH values of the water in the Lake Chilwa Basin are within the maximum permissible limit of 6 to 9 as prescribed for drinking water by WHO (2008) and MBS (2005).

Saka (2006) reported that electrical conductivity(EC) is strongly correlated with sodium ions and the major ions in Lake Chilwa are sodium, chloride and bicarbonates. The latter is responsible for the alkaline pH of the water (8-9).TDS for groundwater, lake water and stream water in the Lake Chilwa Basin range from 553 to 2297 mg/L. As per TDS classification, groundwater and lake water is brackish (TDS >1000 mg/L) watertype whereas streams have fresh water type with TDS < 1000 mg/L (Freeze and Cherry, 1979). Based on the TDS concentration allowed for drinking water, all the groundwater and lake water samples of the Lake Chilwa Basin exceed the prescribed limit of 1000 mg/L (Figure 4). Stream water samples are below the MPL. High TDS concentrations decreases palatability of water and causes gastrointestinal irritation to consumers (Garg et al., 2009).

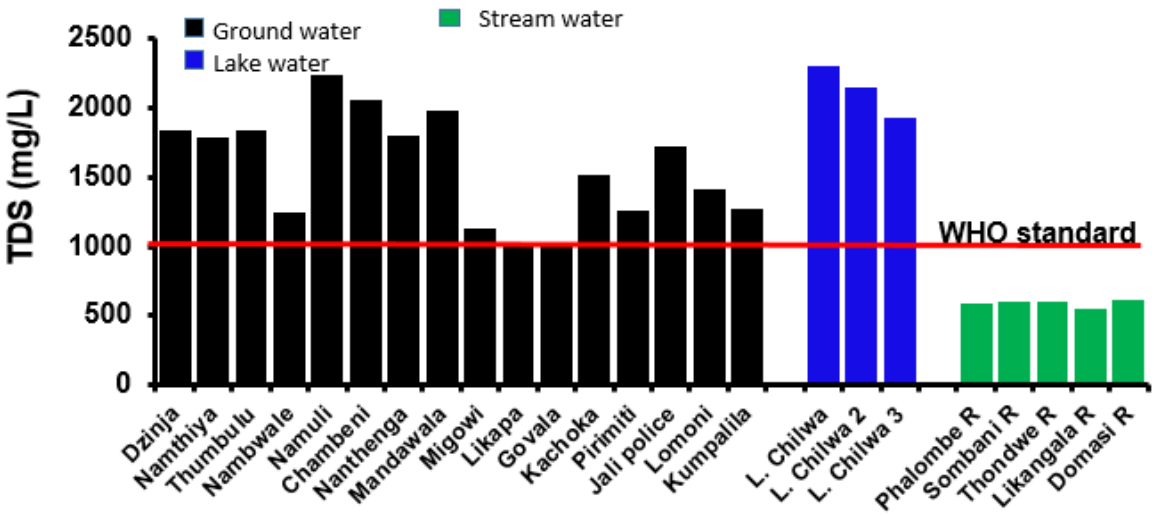


Figure 4: Plot of concentrations of total dissolved solids (TDS) for groundwater and surface water in the Lake Chilwa Basin. Also shown on the plot is a line representing World Health Organization (WHO) maximum permissible concentrations in drinking water (WHO 2008).

According to WHO (2008) and MBS (2005) guidelines, MPL for Na^+ in drinking water is 200 mg/L. Sodium concentrations in all the groundwater and stream water samples are

below the MPL and the concentrations of Na^+ in the lake water samples exceed the MPL (Figure 5a). This is consistent with earlier findings (Saka, 2006). However, Na^+ concentrations are found to be higher than any other cations (Ca^{2+}, Mg^{2+} and K^+) in most samples. The cations Na^+, Ca^{2+}, Mg^{2+} and K^+ are significant constituents of silicate rocks (Freeze and Cherry, 1979) and hence Na^+ in groundwater in the Lake Chilwa Basin is considered to originate from silicate (albite) weathering. A secondary source of Na^+ is halite, concentrated in the soil zone by evaporation and leached into the groundwater by infiltrating rain. Elevated Na^+ concentrations maybe due to dissolution of sodium bicarbonate or albite. Another possible reason for the higher Na^+ concentration could be cation exchange where Ca^{2+} from groundwater is adsorbed on clay materials in exchange of Na^+. Excess Na^+ water makes water unsuitable for drinking because it causes severe health problems like hypertension (Holden, 1970). The concentration of K^+ in groundwater and stream water samples is less than 10 mg/L which is the MPL as per WHO (2008) and MBS (2005). However, the concentration of K^+ in lake waters exceeds the MPL of 10 mg/L (Figure 5b). The low levels of K+ in groundwater could be the consequence of its tendency to be retained in clay minerals and to contribute in the formation of secondary minerals (Zhu and Zhang, 2007). Micas (muscovite and biotite) are major constituents of the sediments / volcanic clastic sediment in the area and therefore responsible for K^+ in the groundwater.

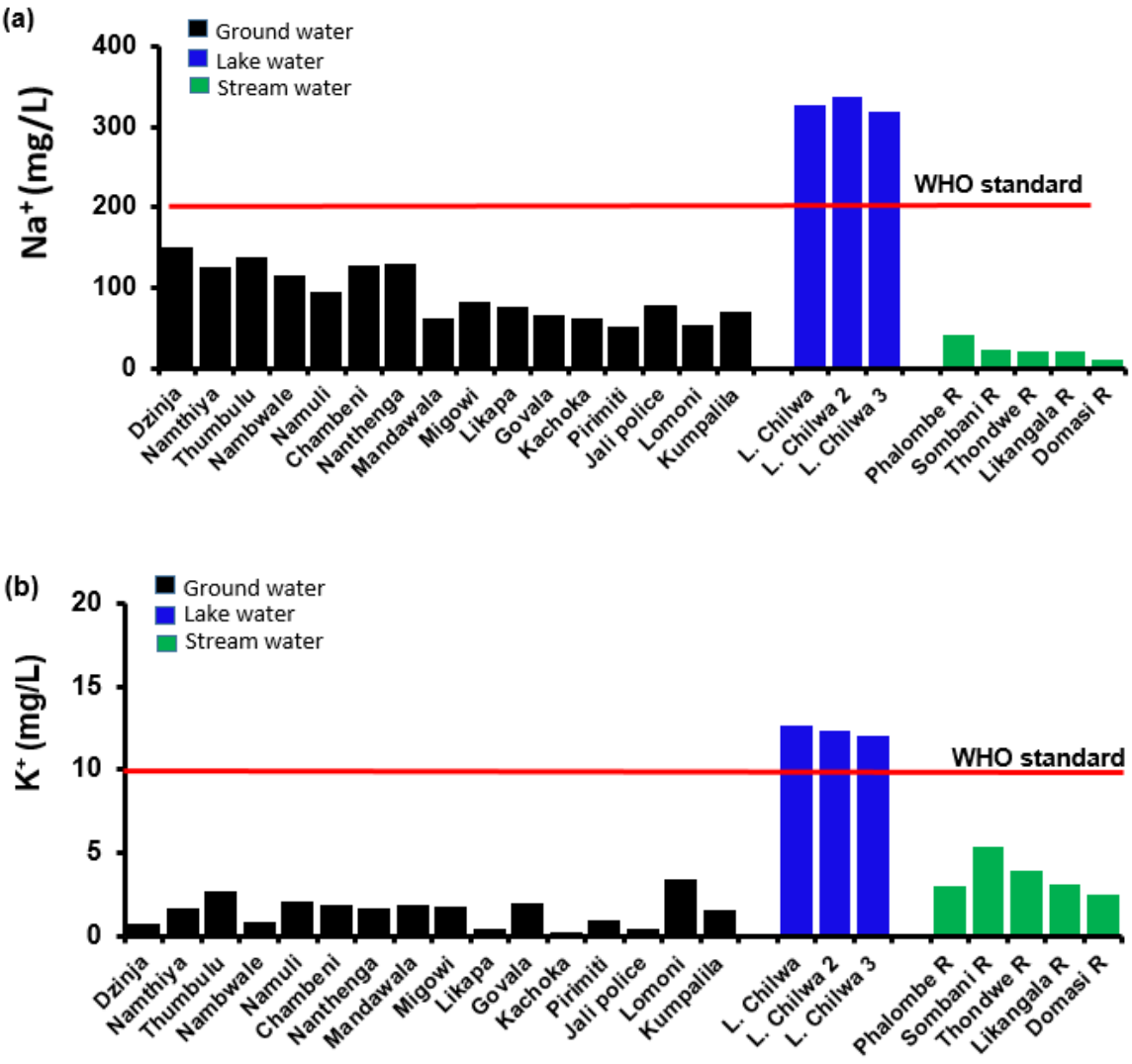


Figure 5*:* Plots of concentrations of cations (a) Na^+ and (b) K^+ for groundwater and surface water in the Lake Chilwa Basin. Also shown on the plot is a line representing World Health Organization (WHO)maximum permissible concentrations in drinking water (WHO, 2008).

The concentration of Mg^{2+} in groundwater, lake water and stream water ranges from 1.3 to 42.1 mg/L and are within the prescribed limit for drinking water specified as 150 mg/L (WHO, 2008; MBS, 2005). The Mg^{2+}in groundwater probably comes from biotite $[K(Mg,Fe)_3(AlSi_3)O_{10}(OH,F)_2]$ and hornblende $[Ca_2(MgFeAl)_5(AlSi)_8O_{22}]$, which are constituents of the aquifers in the study area. All groundwater samples, lake water samples

and stream water samples have Ca^{2+} concentrations below the MPL of 200 mg/L as prescribed by WHO (2008). The Ca-feldspars (anorthite) ($CaAl_2Si_2O_8$) are considered the main source of calcium, releasing Ca^{2+} in the presence of carbonic acid (H_2CO_3) generated in the soil zone. Other possible sources of Ca^{2+} in the groundwaters include dissolution of the mineral hornblende and pyroxenes (Ganyaglo et al., 2017)

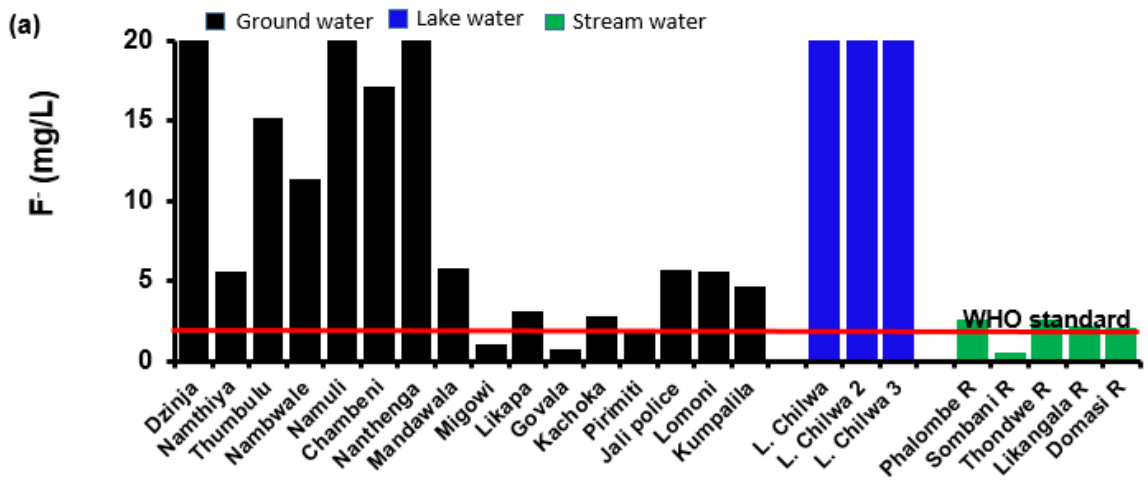
Fluoride may be an essential element for humans (WHO, 2004). Deficiency in drinking water (<0.5 mg/L) leads to dental caries (Edmunds and Smedley, 1996). High intake (>1.5 mg/L) results in physiological disorders, skeletal and dental fluorosis (Latha et al., 1999). Fourteen groundwater samples, all lake water samples and four stream water samples have F^- concentrations that exceed the permissible limit of 1.5 mg/L and 2 mg/L as prescribed by WHO (2008) and MBS (2005), respectively as shown in figure 6(a).Elevated concentrations of F- in groundwater in the Lake Chilwa Basin may be attributed to the dissolution of the mineral apatite (Carter and Bennet, 1973).

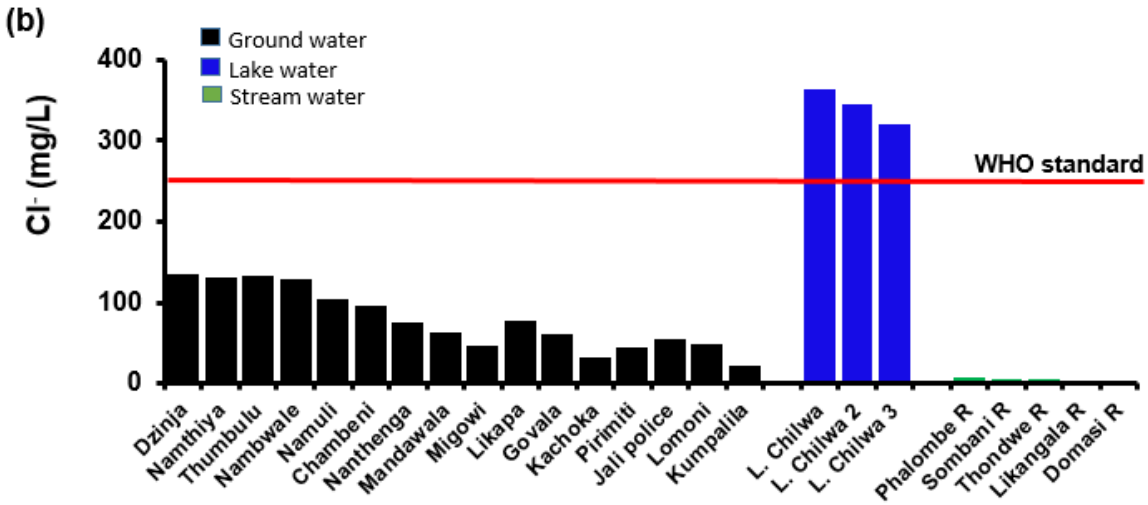
Chloride is considered an important inorganic ion, which deteriorate the quality of drinking water (McCarthy, 2004). High concentrations of Cl^- in drinking water causes a salty taste and has a laxative effect to people not accustomed to it (Bhardwaj and Singh, 2010). Generally, Cl^- is not a significant constituent of silicate rocks. The presence of Cl^- in groundwater and surface water is usually attributed to atmospheric sources, decomposition of organic matter and trace impurities in rocks and minerals (Freeze and Cherry, 1979). All the lake water samples exceeded the MPL of Cl^- for drinking water which is specified at 250 mg/L as per WHO (2008) and MBS (2005) (Figure 6b). All groundwater and stream water samples are below the MPL for Cl^- as specified by WHO (2008).

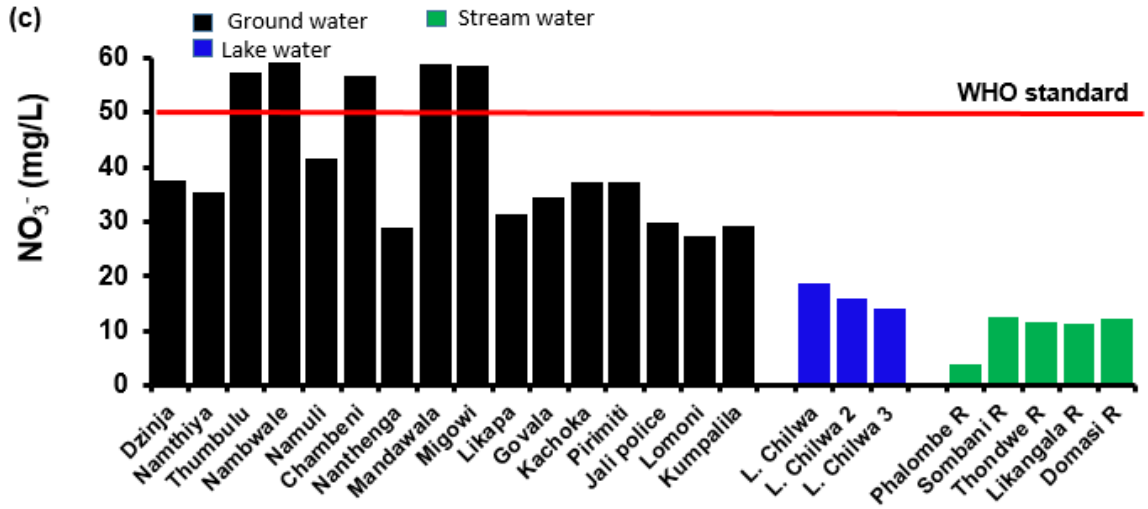
Only five groundwater samples have exceeded the MPL of NO_3^- in drinking water which is specified as 50 mg/L as per WHO (2008) guidelines for drinking water and all stream water and lake water samples have NO_3^- concentration below the WHO (2008) guideline standard (Figure 6c). High concentrations of NO_3^- may be due to the decaying organic matter or sewage and fertilizers used in the catchment (Karnath, 1987).High nitrate intake causes methemoglobinemia in infants, commonly known as "blue baby syndrome" (Comly, 1945). Methemoglobinemia occurs when nitrite (NO_2^-), a reduced form of nitrate, interacts with red blood cells and impairs their ability to carry oxygen (Mirvish, 1991). This impairment results in anoxia (deficiency of oxygen in the blood) and cyanosis (blue blood).

The concentration of SO_4^{2-} is below the MPL of 400 mg/L specified by the WHO (2008) and by MBS(2005) in all the groundwater, lake water and stream water samples. Like Cl^-, SO_4^{2-} is not a major constituent of silicate rocks. The presence of SO_4^{2-} in the aquifer may be explained by the oxidation of pyrite found in the rocks of the area. Higher concentration of SO_4^{2-} in drinking water is associated with respiratory problems (Subba-Rao, 1993).

Bicarbonate (HCO_3^-) is the dominant anion in the study area. Almost all groundwater samples have HCO_3^- concentration exceeding the prescribed limit of 300 mg/L in the drinking water (WHO, 2008) (Figure 6d). All the stream water samples and lake water samples have HCO_3^- concentrations below the MPL of the WHO (2008) standard.


(a)
Ground water
Lake water
Stream water
F- (mg/L)
20
15
10
5
0
WHO standard
Dzinja
Namthiya
Thumbulu
Nambwale
Namuli
Chambeni
Nanthenga
Mandawala
Migowi
Likapa
Govala
Kachoka
Pirimiti
Jali police
Lomoni
Kumpalila
L. Chilwa
L. Chilwa 2
L. Chilwa 3
Phalombe R
Sombani R
Thondwe R
Likangala R
Domasi R


(b)
Ground water
Lake water
Stream water
Cl- (mg/L)
400
300
200
100
0
WHO standard
Dzinja
Namthiya
Thumbulu
Nambwale
Namuli
Chambeni
Nanthenga
Mandawala
Migowi
Likapa
Govala
Kachoka
Pirimiti
Jali police
Lomoni
Kumpalila
L. Chilwa
L. Chilwa 2
L. Chilwa 3
Phalombe R
Sombani R
Thondwe R
Likangala R
Domasi R


(c)
Ground water
Lake water
Stream water
NO3- (mg/L)
60
50
40
30
20
10
0
WHO standard
Dzinja
Namthiya
Thumbulu
Nambwale
Namuli
Chambeni
Nanthenga
Mandawala
Migowi
Likapa
Govala
Kachoka
Pirimiti
Jali police
Lomoni
Kumpalila
L. Chilwa
L. Chilwa 2
L. Chilwa 3
Phalombe R
Sombani R
Thondwe R
Likangala R
Domasi R

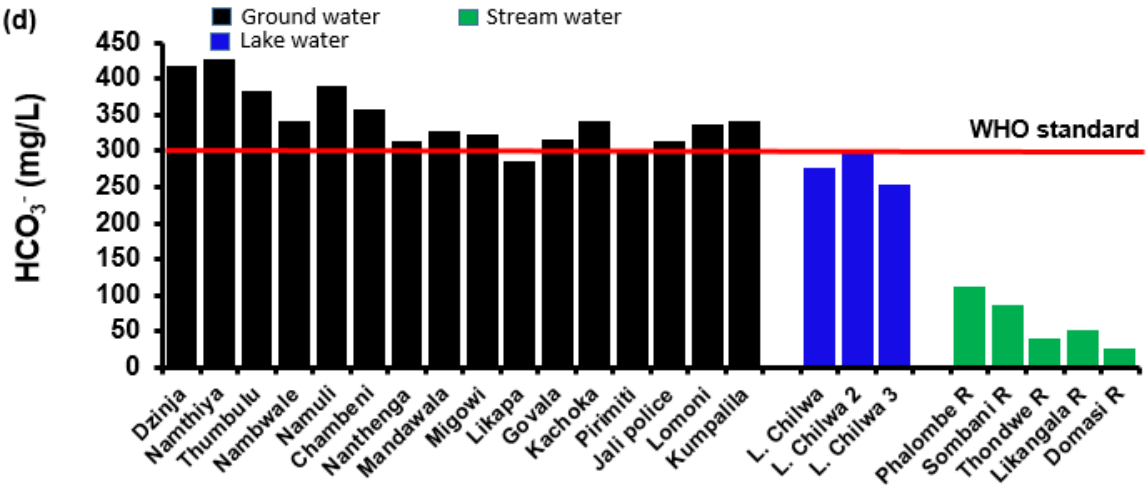


Figure 6: Plots of concentrations of (a) F^- (b) Cl^-, (c) NO_3^-, and (d) $HCO_3^-$for groundwater and surface water in the Lake Chilwa Basin. Also shown on the plots are lines representing World Health Organization (WHO) maximum permissible concentrations in drinking water (WHO, 2008).

5.2 Processes responsible for groundwater and surface water quality

Water quality changes occur from natural water-rock interaction, from solute concentration by evaporation or from anthropogenic pollution. Water-rock interaction and evapo-concentration can be distinguished by evaluating the water for evidence of evaporation. This evidence occurs in the form of enriched stable isotopes of hydrogen and oxygen in water. The δD and $\delta^{18}O$ composition of the groundwater, lake water and stream water samples are shown in Figure 7a. We also show the Global Meteoric Water Line (GMWL; Craig, 1961). We constructed a local evaporation water line (LEWL) based on the surface and lake water samples. The line has the least squares regression defined by the equation:$\delta^2H= 5.7\delta^{18}O +1.1$ and with a regression coefficient(R^2) of0.997 that suggests a meteoric origin. The δD and $\delta^{18}O$ for groundwater are more negative and mostly depleted (-39.0 to -28.0‰; -6.3 to -4.7‰) than stream water (-30.0 to 17.8‰; -5.1 to 2.8‰) and

lake water samples (-7.0 to 33.0‰; 5.5 to 10.0‰). The more positive and enriched δD and $\delta^{18}O$ water in lake water and stream water, and lie on the LEWL, are affected by evaporation(Clark and Fritz, 1997) (Figure 7a). The heavier δD and $\delta^{18}O$ for lake water and stream water is consistent with evaporative enrichment, while in the groundwater samples, there is no evidence of evaporation as they are mostly depleted in stable isotopes and lie on GMWL (Clark and Fritz, 1997). The deviation of the surface water samples from the GMWL to the right indicates that evaporation enrichment of heavy isotope concentrations has occurred, resulting in a slope of 5.7 (Figure 6a); somewhat less than the GMWL slope(Faye, et al., 2005; Asfaw, 2010). The surface water samples are characterized by comparatively high chloride concentrations. Therefore, evaporation had an impact on the Lake Chilwa water salinity in the study area. Evaporation leads to concentration of salts (NaCl) making the water more salty (Morgan and Kalk, 1968; Saka, 2006).

To evaluate the effect of evaporation on evapo-concentration of solutes, we plot the TDS vs. $\delta^{18}O$ (Figure 7b).Enriched $\delta^{18}O$ and high TDS can be attributed to evapo-concentration (e.g. Atekwana et al., 2016). There is evidence of evapo-concentration in lake water samples with high TDS and $\delta^{18}O$. However, no evaporation was observed in groundwater samples hence no evidence of evapo-concentration effect on solute. Our results indicate that groundwater with high TDS and low $\delta^{18}O$ can result from water-rock interaction.

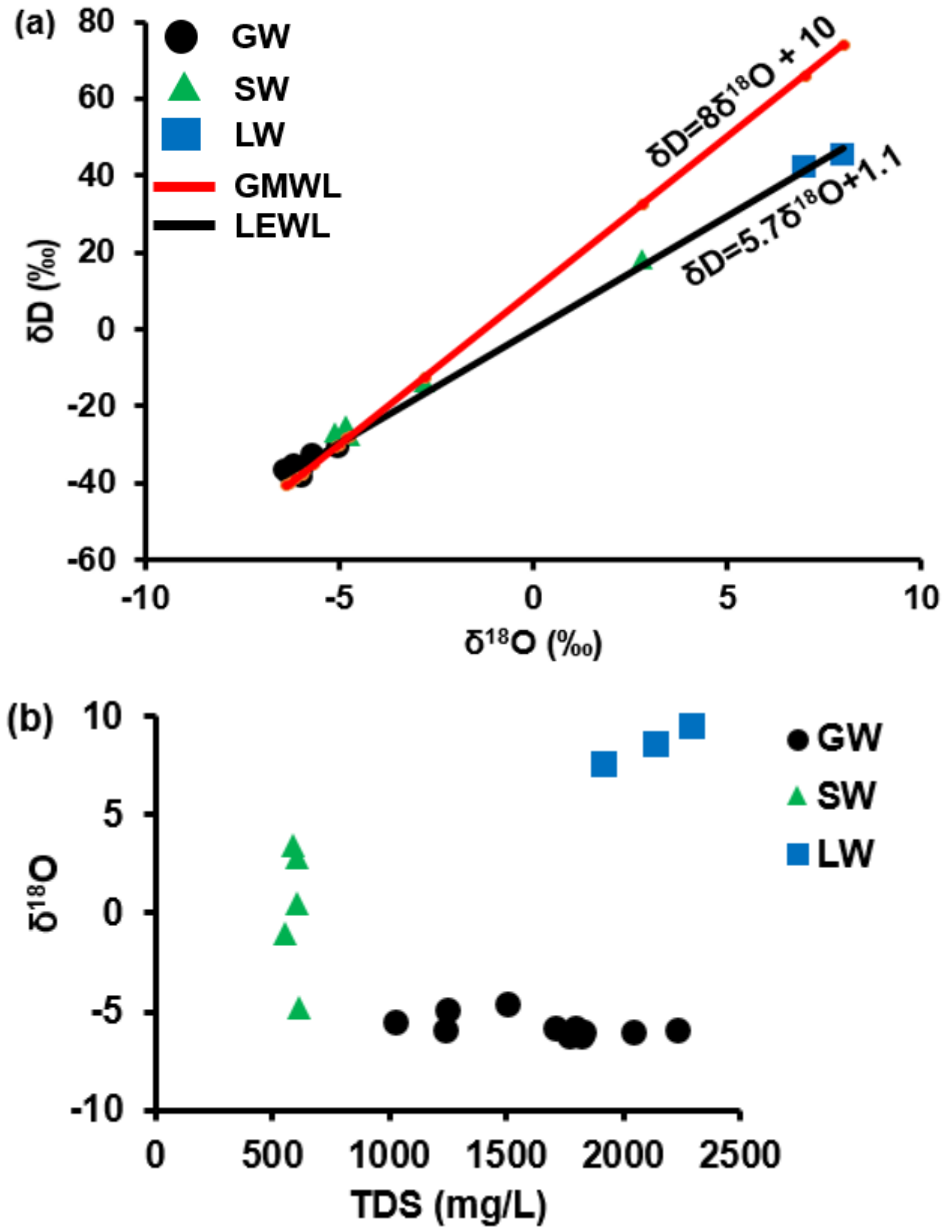


Figure 7: Cross plot of isotopic composition of (a) oxygen ($\delta^{18}O$) vs. hydrogen ($\delta^{2}H$).Also plotted is the Global Meteoric Water Line (GMWL) and the local evaporation water line (LEWL) and (b) Cross plot of isotopic composition of Total dissolved solids (TDS) vs. $\delta^{18}O$.for groundwater and surface water in the Lake Chilwa Basin.

5.3 Ionic evolution of groundwater and surface waters

The piper diagram (Figure 8) shows the relative proportions of cations and anions of three distinct water types shown in grouping. The water types have facies of : (A) Na+K-HCO3, (B) Na+K-Cl, and (C) Ca-Mg-Na+K-HCO3-Cl. Water type A consists of all stream water samples and show a range of 70 to nearly 90% Na+K and the anions are predominantly HCO3 > 80%. Watertype B consists of lake water and have Na + K between 90 and 100% and anion facies dominated by Cl of 60 to 70%. Watertype C consists of groundwater and is a mixed cation and mixed anion facies and has Ca^{2+}, Mg^{2+}, Na^{+} + K^{+} in the cation facies and mainly HCO_3^{-} and Cl^{-} in the anion faces. The cation faces has the following composition: 40 to 80% Ca, 10 to 35% Mg and 30 to 50% Na + K, whereas, the composition of the anion facies is 60 to nearly 90% HCO_3 and 10 to 40% Cl.

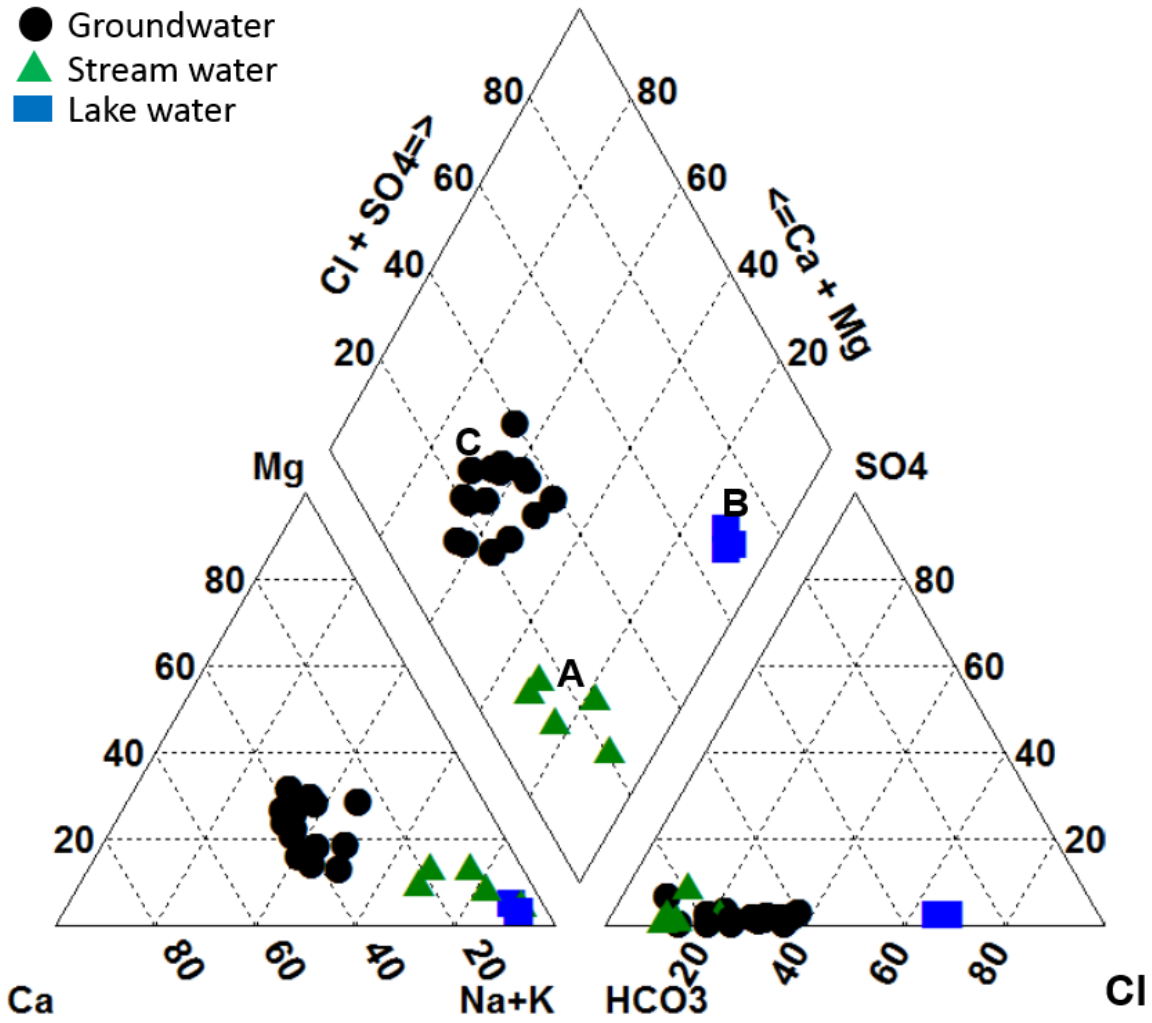


Figure 8: Piper plot showing ionic proportions for groundwater and surface water in the Lake Chilwa Basin

The chemical evolution of groundwater in crystalline basins can be attributed to water-rock interactions involving weathering of silicate minerals by $CO_{2(g)}$. From previous studies, silicate weathering and carbonate dissolution are viable processes controlling the variations in water quality (Wanda et al., 2013; Mapoma et al., 2016). Plagioclase weathering is probably the most important process that controls groundwater composition in the crystalline rocks resulting from the weathering of two major minerals: anorthite (An) and

albite (Ab) (e.g., Stober and Bucher, 1998). Weathering of plagioclase leads to an increase of Ca^{2+}, Na^{+}, HCO_3^{-} and SiO_2 concentrations in groundwater (Petrides et al., 2006). Weathering of anorthite, a component of plagioclase feldspar in the presence of $CO_{2(g)}$ can be written as:

$$3H_2O + 2CO_2 + CaAl_2Si_2O_8 \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^{-} \quad (1)$$

Anorthite Kaolinite

A plot of Ca^{2+} vs. HCO^{3-} presented in Figure 9 shows a 1: 2 relation for Ca^{2+} vs. HCO_3^{-} for the groundwater samples indicating that Ca^{2+} and HCO^{3-} are likely derived from the weathering of anorthite. For the lake water and stream water samples, they do not fall on the 1:2 ratio, hence, there must be other minerals that are weathered to produce these waters or the chemical evolution of groundwater may explain their chemistry. However the data points are not in a straight line indicating that there must be contribution of other minerals.

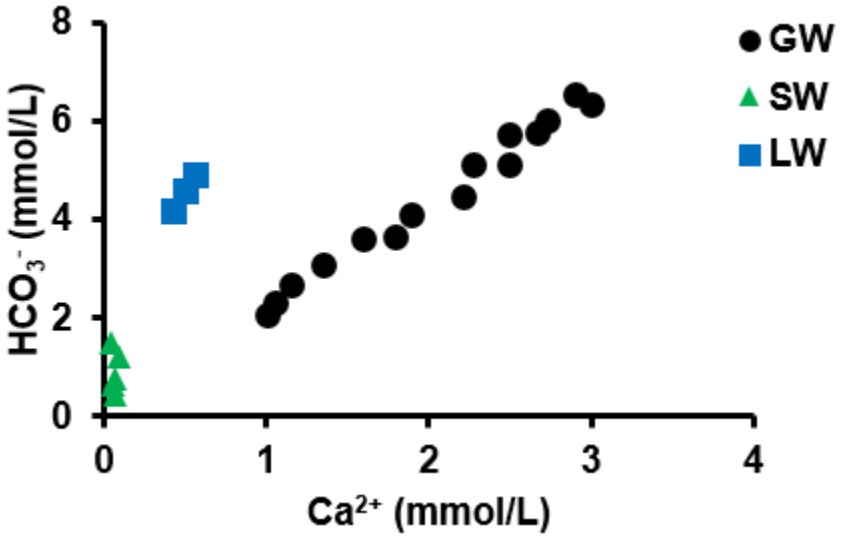


Figure 9: Cross plots of Ca^{2+} vs. HCO_3^{-} for groundwater and surface water in the Lake Chilwa Basin.

Based on the mineralogy of the crystalline basement in the Lake Chilwa Basin, there are additional weathering reactions that can explain the concentrations of the cations in the groundwater. Granite which is one of the major rocks in the basin can contain either Na – rich, Ca – poor plagioclase or may have high Ca and Na poor minerals (Mast and Drever, 1990). The Ca-dominated water type can best be understood if plagioclase dissolves incongruently (Eq. 2):

$$3H_2O + 2CO_2 + Na_4CaAl_6Si_4O_40 \rightarrow Al_2Si_2O_5(OH)_4 + 4NaAlSi_3O_8 + Ca^{2+} + 2HCO_3^- \quad (2)$$

Plagioclase Kaolinite Albite

This is albitization of feldspar and secondary albite replaces plagioclase. The reaction (Eq. 2) is a description of plagioclase weathering in calcite under-saturated environments.

Weathering of biotite, which is the most abundant FeMg-mineral in most granite and gneisses of the basement, and hornblende contributes Mg and K to the solutes in waters (Mark and Bucher, 1997). At the elevated temperatures and pressures of the continental burial setting, dolomite form by reaction of calcite and magnesium silicate (Compton, 1980). The reaction proceeds as:

$$\frac{1}{5}Mg_5Al_2Si_3O_{10}(OH)_8 + \frac{4}{5}Al_2Si_2O_5(OH)_4 + 2CaCO_3 \rightarrow CaMg(CO_3)_2 + CaAl_2Si_2O_8 + \frac{1}{5}SiO_2 + \frac{12}{5}H_2O \quad (3)$$

Figure 10 shows a 1:2 relation indicating the dissolution of dolomite in the groundwater. Dolomite dissolution is represented by the equation:

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (4)$$

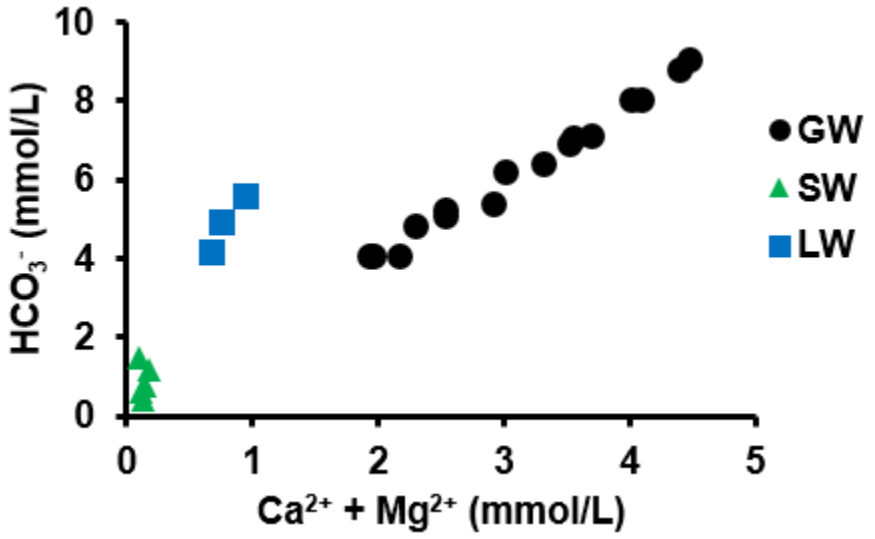


Figure 10: Cross plots of Ca^{2+} + Mg^{2+} vs. $HCO_3^-$for groundwater and surface water in the Lake Chilwa Basin.

As the reaction progresses, water will evolve and become eventually saturated with respect to calcite. An alternative to reaction (Eq. 2) is the process of sericitization of plagioclase which produces Na – rich mica as a product (Blum and Stillings, 1995).

$$2H_2O + 2CO_2 + Na_4CaAl_6Si_4O \rightarrow NaAlSiO_{10}(OH)_2 + 3NaAlSi_3O_8 + 2SiO_2 + Ca^{2+} + 2HCO_3^- \quad (5)$$

The high Ca waters could be derived by preferential weathering of anorthite rich plagioclase in more mafic rocks with low X_{Na} (or Ab) such as amphibolites and mafic gneisses.

Stream water samples can be explained by weathering of minerals in the study area. There is general increase in the silica concentrations and the dominance of Na+K in the cation facies and HCO_3 in the anion faces of stream samples which can be explained by the

weathering of sodium and potassium rich silicates (Stallard and Edmond, 1987). For example, albite is a sodium feldspar weathers as described by the following equation:

$$2NaAl_2Si_3O_8 \text{ (albite)} + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3^- \quad (6)$$

Figure 11 shows a 1: 1 relation between Na^+ and HCO_3^- in stream water samples indicating weathering of sodium feldspar minerals. Ground water samples and lake water samples do not show a 1: 1 relationship therefore have other processes controlling their ionic evolution (Jalali, 2006).

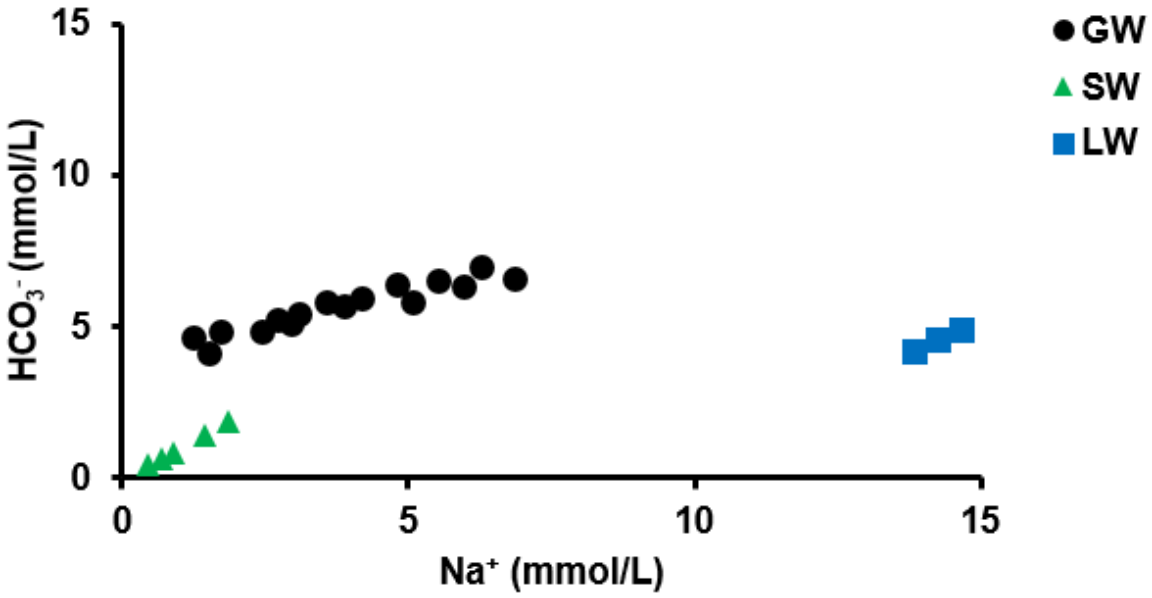


Figure 11: Cross plot of Na^+ vs. HCO_3^- for groundwater and surface water in the Lake Chilwa Basin.

Alternatively, since groundwater discharges to streams to support base flow, then the difference between groundwater and stream water can be explained by chemical evolution in the stream channel. For the concentrations of Ca^{2+} and Mg^{2+} to decrease in the stream

water, calcite and dolomite can be precipitated. However, the equilibrium state of stream water is such that it is under-saturated as $SI_{calcite}$ and $SI_{dolomite}$ is <<0 (Table 2).

5.4 Carbonate evolution of groundwater and surface water

Carbonate evolution in the lake Chilwa Basin is unlikely to be influenced by the weathering of carbonates. Carbonate are not abundant in the aquifer rocks nor is it a major component of the rocks in the basin. However, during the weathering and evolution of groundwater in aquifers dominated by silicates, carbonate evolution influences how the water composition changes. For example, feldspar reacts with dilute meteoric water and forms an insoluble residual Al-silicate mineral and a Ca-HCO_3 water. The weathering of the feldspar proceeds until the solution is saturated with respect to the carbonate minerals(calcite and dolomite). From then on, plagioclase weathering reaction (Eq. 1) and the calcite equilibrium hold simultaneously:

$$2H_2O + CO_2 + CaAl_2Si_2O_8 \rightarrow Al_2Si_2O_5(OH)_4 + CaCO_3 \quad (7)$$

Anorthite Kaolinite Calcite

where the $CaCO_3$ is formed by the reaction:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \quad (8)$$

The supersaturation of groundwater with respect to carbonates causes calcite to precipitate in fractures and cavities and if this occurs in significant volume, may be the source of Carbonate minerals. Secondary calcite is present in fractures, veins and cavities of the granite and gneisses in the Lake Chilwa Basin (Stober and Bucher, 1998).

The amount of Ca^{2+} and HCO_3^- that can be dissolved in the water largely depends on the availability of CO_2. If the rocks contain carbonates and the water is not saturated with respect to calcite reaction (Eq. 9) or dolomite reaction (Eq.4) will occur and equilibrium will be reached:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \quad (9)$$

The saturation state of the groundwater, surface water and groundwater is shown in Figure 12. Only groundwater appears to be close to equilibrium with both calcite (Figure 12a) and dolomite (Figure 12b). As the concentrations of Ca^{2+} or $Ca^{2+} + Mg^{2+}$ increases in groundwater, the samples approach equilibrium saturation with respect to calcite (Figure 12 a) and dolomite (Figure 12 b).

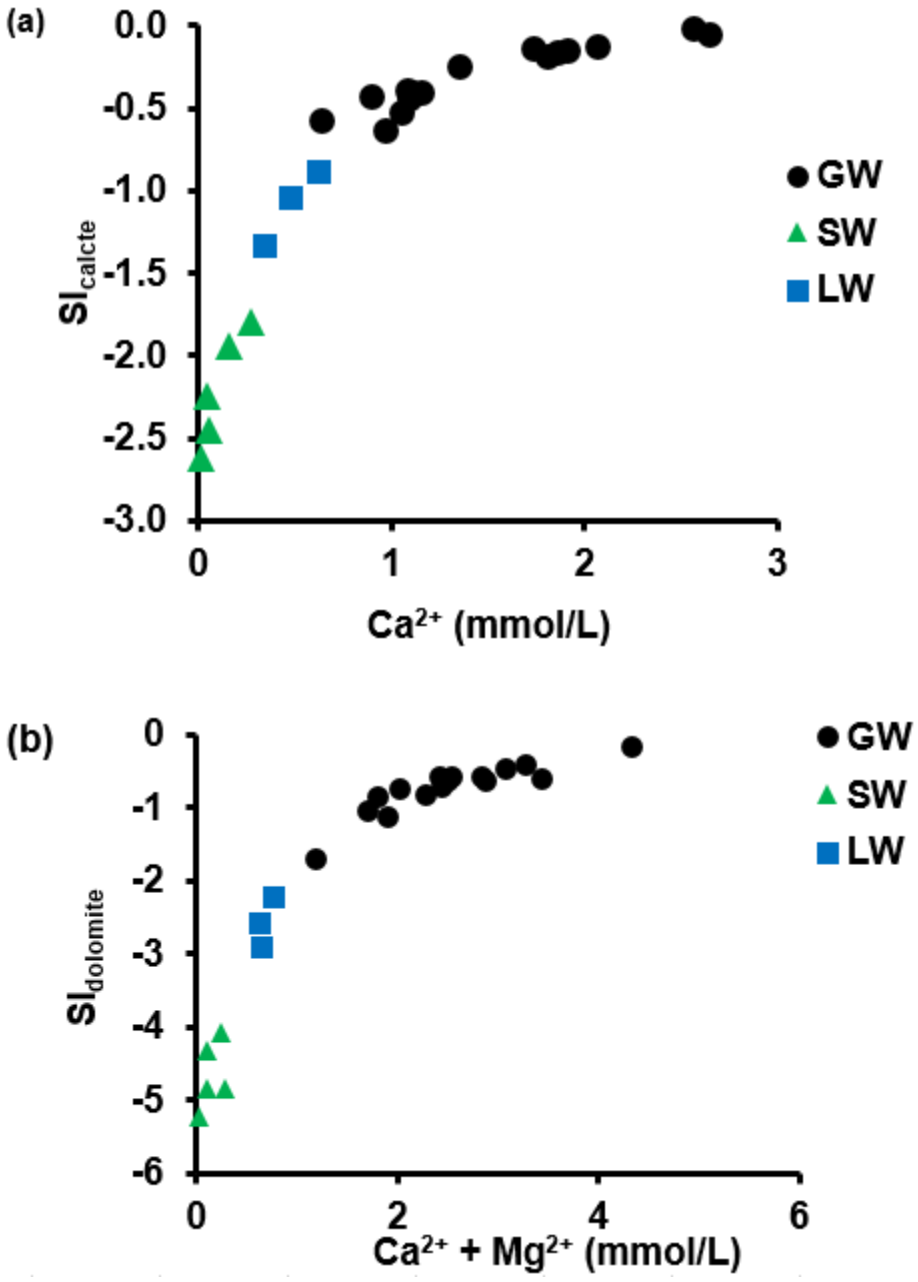


Figure 12:Cross plots of (a) Ca^{2+} vs the saturation index for calcite ($SI_{calcite}$) and (b) Ca^{2+} + Mg^{2+} vs. saturation index for dolomite ($SI_{dolomite}$)for groundwater and surface water in the Lake Chilwa Basin.

The concentration of CO_2 (pCO_2) in the groundwater is extremely low (log pCO_2 = -5.5 to -3.9). This is evidence that the ability of the groundwater to both weather silicates or

carbonated is greatly diminished. Thus, although there is the possibility of weathering carbonated from cavities and fractures in the lake Chilwa Basin, it is likely that the major cations are dominated by silicate weathering. A plot of pH vs. pCO_2 in Figure 13 shows increase in pH with decrease in pCO_2 which suggests that weathering has consumed the CO_2 in a "closed system" evolution where CO_2 is not continuously replenished as weathering proceeds (Drever, 1977).

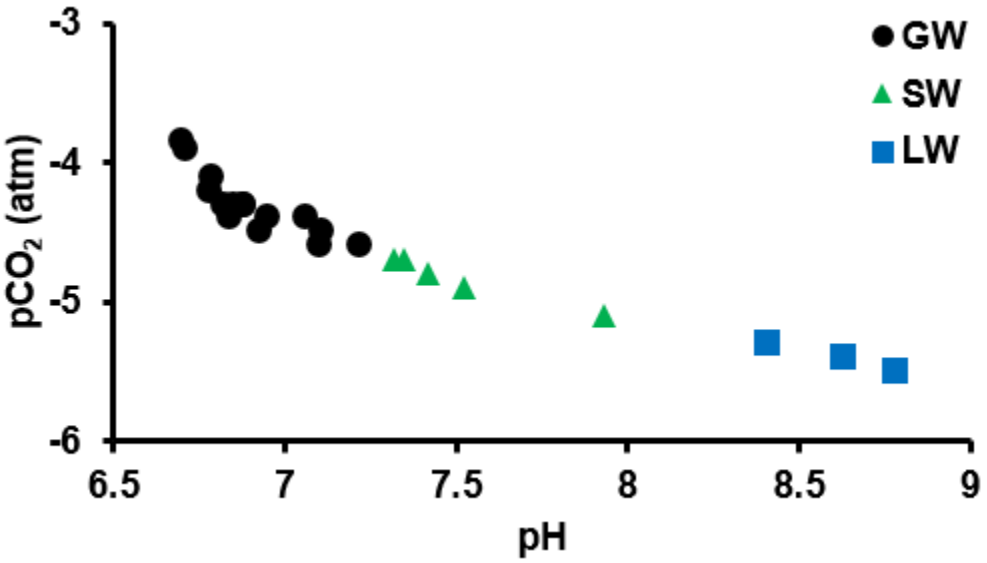


Figure 13:Cross plot of pH vs. pCO_2 of for groundwater and surface water in the Lake Chilwa Basin

CHAPTER 6

6.0 Conclusions

Hydrochemical analysis revealed that all groundwater and Lake Chilwa water in the Lake Chilwa Basin are brackish. The pH are slightly acidic, but mostly alkaline in nature. The major processes controlling the water quality in the Lake Chilwa Basin varies in relation to the type of water reservoir. Water-rock interaction involving weathering of silicates control the major ions such as calcium, sodium and magnesium in groundwater, whereas, evaporation is the dominant factor leading to poor water quality in the water from Lake Chilwa.

Bicarbonate (HCO_3^-) is the dominant anion in the study area. Almost all groundwater samples have HCO_3^- concentration exceeding the prescribed limit of 300 mg/L in drinking water (WHO, 2008). The occurrence of Ca^{2+} and HCO_3^- in groundwater causes the salty condition. The most common salt of bicarbonate is calcium bicarbonate ($Ca(HCO_3)_2$). In particular, $Ca(HCO_3)_2$ contributes to TDS, a common parameter for assessing water quality. Lake Chilwa waters are mostly classified as sodium chloride whereas stream waters are sodium bicarbonate. Elevated Na^+ concentrations may be due to evaporation and probably cation exchange where Ca^{2+} is adsorbed on clay minerals in exchange for Na^+.

Notable characteristics of the water include high EC and high concentrations of TDS, HCO_3^-, Cl^-, F^- and Ca^{2+} in groundwater and lake water. Failure of these parameters (e.g., TDS, HCO_3^-, Cl^-, F^- and Ca^{2+}) to comply with the WHO or MBS guidelines standards for drinking water signify that the some of the groundwater and lake water are of poor quality and unacceptable for human consumption without treatment.

Therefore, in general, the groundwater geochemistry of the Lake Chilwa Basin is principally controlled by water-rock interaction involving dissolution and precipitation of minerals, whereas, that of surface water, especially Lake Chilwa is controlled by evaporation and cation exchange.

CHAPTER 7

7.0 Future work

The conclusions drawn from this study are the results of water chemical analysis, conducted in rainy season in Lake Chilwa Basin in Malawi. More frequent sampling (e.g., weekly to monthly) and analysis of the groundwater and surface water in the basin would allow observation of seasonal changes and assess if seasonality plays a role in the geochemical evolution of groundwater and surface water. Scouting additional boreholes, streams and various places of water points on Lake Chilwa to increase the sapling density. Conducting measurements for δD and $\delta^{18}O$ and stable carbon isotopes ($\delta^{13}C$) can be used to create a more robust data set. Determining the age of the water using 14-C, would allow models to be created that assess time scale of water evolution and circulation.

The results from this study could assist decision makers understand the effects of seasonal changes on water resources and be able to apply water treatment options at the appropriate times.

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APPENDICES

Table showing charge balance, alkalinity, SI fluorite, and SI halite

Sample ID	Station ID	Charge balance (%)	$SI_{fluorite}$	SI_{halite}
Pt 1 BH	Dzinja	1.97	1.92	-6.35
Pt 2 BH	Namthiya	3.21	0.64	-6.41
Pt 3 BH	Thumbulu	0.67	1.43	-6.33
Pt 4 BH	Nambwale	3.77	1.22	-6.5
Pt 5 BH	Namuli	-0.87	2.01	-6.6
Pt 6 BH	Chambeni	4.44	1.47	-6.49
Pt 7 BH	Nanthenga	4.74	2.3	-6.63
Pt 8 BH	Mandawala	2.06	0.48	-7
Pt 9 BH	Migowi	3.28	-0.91	-6.98
Pt 10 BH	Likapa	3.38	-0.02	-6.84
Pt 11 BH	Govala	2.9	-1.19	-6.96
Pt 12 BH	Kachoka	1.63	-0.22	-7.26
Pt 13 BH	Pirimiti	4.31	-0.49	-7.13
Pt 14 BH	Jali police	-3.01	0.25	-6.95
Pt 16 BH	Lomoni	-1.87	0.46	-7.16
Pt 17 BH	Kumpalila	4.9	0.25	-7.4
Pt 1 SW	L. Chilwa	-3.26	1.64	-5.52
Pt 7 SW	L. Chilwa 2	-2.67	1.65	-5.53
Pt 8 SW	L. Chilwa 3	-1.33	1.62	-5.58
Pt 2 SW	Phalombe R	0.31	-1.57	-7.99
Pt 3 SW	Sombani R	0.44	-2.18	-8.34
Pt 4 SW	Thondwe R	0.99	-1.43	-8.39
Pt 5 SW	Likangala R	-1.16	-1.55	-8.64
Pt 6 SW	Domasi R	-2.97	-1.52	-9.11

VITA

Type Full Name Here

Candidate for the Degree of

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- Proficiency in AQUACHEM software developed specifically for graphical, numerical and modelling of water quality data.
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Professional Memberships:

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